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TITLE: M<sup>III</sup>N based materials and methods and apparatus for producing same

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Abstract Paragraph - ABTX (1):

A high deposition rate sputter method is utilized to produce bulk, single-crystal, low-defect density Group III nitride materials suitable for microelectronic and optoelectronic devices and as substrates for subsequent epitaxy, and to produce highly oriented polycrystalline windows. A template material having an epitaxial-initiating growth surface is provided. A Group III metal target is sputtered in a plasma-enhanced environment using a sputtering apparatus comprising a non-thermionic electron/plasma injector assembly, thereby to producing a Group III metal source vapor. The Group III metal source vapor is combined with a nitrogen-containing gas to produce a reactant vapor species comprising Group III metal and nitrogen. The reactant vapor species is deposited on the growth surface to produce a single-crystal M<sub>sup</sub>.IIIN layer thereon. The template material is removed, thereby providing a free-standing, single-crystal M<sub>sup</sub>.IIIN article having a diameter of approximately 0.5 inch or greater and a thickness of approximately 50 microns or greater.

Summary of Invention Paragraph - BSTX (2):

[0001] The present invention is generally directed to the production of Group III metal nitride materials for use as free-standing articles as well as substrates for further processes and/or microelectronic and optoelectronic devices. In particular, the present invention is directed to the production of low-defect density, single-crystal materials and highly-oriented polycrystalline materials utilizing enhanced sputtering techniques.

Summary of Invention Paragraph - BSTX (7):

[0005] Accordingly, homoepitaxial growth of GaN thin films on bulk GaN substrates is of great interest. The use of GaN substrates would eliminate the problems due to lattice mismatch and thermal expansion mismatch. Unfortunately, the availability of GaN substrates has been limited due to conventional processing capabilities. This problem has hindered the development of devices based on GaN and related nitride semiconductors. Several obstacles exist to the successful manufacturing and commercializing of

high device-quality Group III nitride-based materials, whether in bulk, single-crystal, polycrystalline or epitaxial form, for electronics and other applications. These obstacles generally include cost, reproducibility, and purity.

Summary of Invention Paragraph - BSTX (9):

[0007] Currently, aluminum nitride and gallium nitride exist only as polycrystalline or powder forms, or in thin films. Polycrystalline bulk aluminum nitride can be manufactured using powder processing techniques. This process has not yielded semiconductor-grade single crystal material. Formidable problems are associated with such techniques, beginning with the production of pure aluminum nitride powders and then the sintering of oxygen-free and defect-free aluminum nitride. Some of these problems include the production of both high-purity and uniform particle-size powders. The highest purity powders can contain up to 1% of oxygen and binders, such as  $Y_2O_3$ , that are needed to produce aluminum nitride with a high density. Therefore, high density is achievable at the expense of contamination. Sintering of these aluminum nitride powders is also a difficult process. The covalent nature of aluminum nitride prevents densification of pure aluminum nitride at low temperatures. Aluminum nitride decomposes at high temperatures, such as above 1600.degree. C., thereby preventing densification. Hence, costly sintering aids such as high pressures and impurities are required for producing high-density material. Other problems associated with powder processing of aluminum nitride include maintaining the purity and integrity of the powder, controlling the environment at high sintering temperatures, and the production of defect-free parts. Aluminum nitride is very difficult to manufacture using powder processing techniques without introducing contamination that will have adverse effects on the optical and thermal properties of the material. These impurities can be present in the crystalline lattice structure, and can migrate to the grain boundaries during sintering, causing the infrared absorbance to be high.

Summary of Invention Paragraph - BSTX (14):

[0011] According to one method of the present invention, a single-crystal M<sub>III</sub>N article is produced. A template material having an epitaxial-initiating growth surface is provided. A Group III metal target is sputtered in a plasma-enhanced environment to produce a Group III metal source vapor. The Group III metal source vapor is combined with a nitrogen-containing gas to produce reactant vapor species comprising the Group III metal and nitrogen. The reactant vapor species is deposited on the growth surface to produce a single-crystal M<sub>III</sub>N layer thereon. The template material is removed, thereby providing a free-standing, single-crystal M<sub>III</sub>N article

having a diameter of approximately 0.5 inch or greater and a thickness of approximately 50 microns or greater.

Summary of Invention Paragraph - BSTX (21):

[0018] Therefore, according to another method of the present invention, a single-crystal M.sup.IIIN article is produced by using a sputtering apparatus comprising a non-thermionic electron/plasma injector assembly to produce the Group III metal source vapor from a Group III metal target. The Group III metal source vapor is combined with a nitrogen-containing gas to produce reactant vapor species comprising Group III metal and nitrogen. The reactant vapor species is deposited on the growth surface of the template material to produce a single-crystal M.sup.IIIN layer thereon.

Summary of Invention Paragraph - BSTX (25):

[0022] According to one embodiment of the present invention, a bulk single-crystal M.sup.IIIN article has a diameter of approximately 0.5 inch to approximately 12 inches and a thickness of approximately 50 microns or greater.

Summary of Invention Paragraph - BSTX (26):

[0023] According to another embodiment of the present invention, a single-crystal M.sup.IIIN article is produced in wafer form, having a thickness ranging from approximately 50 microns to approximately 1 mm.

Summary of Invention Paragraph - BSTX (27):

[0024] According to yet another embodiment of the present invention, a single-crystal M.sup.IIIN article is produced in boule form, having a diameter of approximately 2 inches or greater and a thickness ranging from approximately 1 mm to greater than approximately 100 mm.

Summary of Invention Paragraph - BSTX (28):

[0025] According to still another embodiment of the present invention, the single-crystal M.sup.IIIN layer is used as a seed crystal, such that additional reactant vapor species comprising the Group III metal and nitrogen can be deposited the M.sup.IIIN layer to produce a bulk, homoepitaxially grown M.sup.IIIN article.

Summary of Invention Paragraph - BSTX (30):

[0027] The single-crystal M.sup.IIIN layers or articles produced according to the methods of the present invention can be formed at a growth rate greater than approximately 10 microns/hour.

Summary of Invention Paragraph - BSTX (34):

[0031] It is therefore an object of the present invention to provide low-defect density, single-crystal Group III nitride articles, substrates and device layers characterized by purities and sizes that previously have been unattainable.

Detail Description Paragraph - DETX (5):

[0064] As used herein, the term "epitaxy" generally refers to the formation of a single-crystal film structure on top of a crystalline substrate. Epitaxy can be broadly classified into two categories, namely homoepitaxy and heteroepitaxy. In the case of homoepitaxy, the film and the underlying substrate have the same structural relationships. Reasons for extending the substrate through the deposition thereon of an epitaxial film layer, or "epilayer," of the same composition include the observations that the epitaxial layer (1) is typically much more free of defects as compared to the substrate, (2) is typically purer than the substrate, and (3) can be doped independently of the substrate. The respective lattice parameters of the epilayer and substrate are perfectly matched, with no interfacial bond straining.

Detail Description Paragraph - DETX (8):

[0067] Referring now to FIG. 1, a heterostructure, generally designated 10, is illustrated according to the invention. Heterostructure 10 comprises a base substrate 12 on which a single-crystal, low-defect density M.sup.IIIN layer 14 is epitaxially grown. Preferably, base substrate has a diameter of 0.5 inch or greater. Base substrate 12 has a growth surface 12A having a composition and structure that enables base substrate 12 to serve as a template for the epitaxial growth of M.sup.IIIN layer 14 thereon. Alternatively, a buffer layer or interlayer 16 is grown on base substrate 12 so as to provide a suitable epitaxy-initiating growth surface 16A for M.sup.IIIN layer 14.

Detail Description Paragraph - DETX (12):

[0071] According to one method of the invention, base substrate 12 and a Group III metal target are loaded into a sputter deposition chamber. A highly energetic plasma-enhanced environment is generated in the chamber, using a suitable background gas such as argon. Separate nitrogen-containing source gas is conducted into the chamber. Alternatively, the gas utilized to generate the plasma could also be used as the reactant source gas, in which case the background gas provides the nitrogen species. The Group III metal target is sputtered to produce a Group III metal source vapor. The Group III metal source vapor combines with the nitrogen-containing gas, which is characterized as including one or more species such as diatomic nitrogen, atomic nitrogen, nitrogen ions, and partially ionized nitrogen, as well as nitrogen-containing compounds such as ammonia. As a result, reactant vapor species comprising

components of the Group III metal and the nitrogen are produced within the reaction chamber, and are deposited on growth surface 12A of base substrate 12 (or on growth surface 16A when first depositing buffer layer 16). The as-deposited reactant vapor species grows epitaxially on growth surface 12A to produce single-crystal M.sup.IIIN layer 14. M.sup.IIIN layer 14 can be doped by conducting conventional doping methods, such as by introducing dopant-containing gases into the reaction chamber under controlled conditions.

Detail Description Paragraph - DETX (14):

[0073] Referring to FIG. 2, upon completion of the substrate removal process, a bulk, free-standing, single-crystal M.sup.IIIN article 20 is produced. In accordance with the invention, article 20 has a diameter d of 0.5 inch or greater, a thickness t of 50 microns or greater, and a defect density of no greater than 10.sup.9 defects/cm.sup.3. Article 20 can be doped according to known methods. In the production of alloys and compounds, the resulting composition can have greater than 50% Group III metal and nitrogen components.

Detail Description Paragraph - DETX (24):

[0083] Referring to FIG. 5A, another heterostructure, generally designated 40, is illustrated according to the invention in which a lateral epitaxial overgrowth method is implemented. In this embodiment, interlayer 16 and/or an additional interlayer 18 (which can have a composition different from that of interlayer 16) is deposited on base substrate 12, and is then patterned using a conventional masking and/or etching technique to form a patterned (for example, striped) layer 42. Using the enhanced sputtering technique described herein, a reactant vapor species comprising Group III metal and nitrogen components is then transported toward patterned layer 42 and exposed portions 42A of layer 42. A device-quality, bulk single-crystal M.sup.IIIN layer 44 begins to grow upwardly from exposed portions 42A of layer 42, and then grows laterally over the tops of patterned layer 42. Upon continued growth of M.sup.IIIN layer 44, the growing crystal coalesces to form a continuous, low-defect density layer.

Detail Description Paragraph - DETX (50):

[0109] Traditionally, sputter-deposited films have been plagued with low reactive sputter rates, excessive stress, and poor crystalline growth. Due to the non-contaminating nature of transport device 100 or 200, however, the hollow cathode effect can be advantageously utilized to produce both single-crystal and highly-oriented polycrystalline, bulk-form substrates, such as those described hereinabove, at lower pressures, ultra-high deposition rates, and with minimal material stress. Transport device 100 or 200 is also capable of growing epitaxial layers on substrates. Examples of deposited

materials include binary, tertiary, and quaternary Group III nitride based compounds such as aluminum nitride, gallium nitride, indium nitride, aluminum gallium nitride, indium gallium nitride and aluminum indium gallium nitride, and alloys thereof. Suitable dopants can be added during the growth process. Both single-crystal and polycrystalline morphologies are obtainable. In one specific example, transport device 100 or 200 is capable of growing aluminum nitride purer than that made by powder processing methods and faster than CVD methods. Moreover, because transport device 100 or 200 exhibits a very high degree of sputter particle ionization, transport device 100 or 200 produces a plasma beam environment that facilitates the synthesis of nitride based materials. The material grown by transport device 100 or 200 exhibits the bulk properties of nitrides due to the resulting high crystallinity and purity. In particular, bulk aluminum nitride produced from transport device 100 or 200 has a high IR and UV transmittance, a high thermal conductivity, and a high degree of c-axis orientation.

Detail Description Paragraph - DETX (60):

[0118] An example of a method for manufacturing a GaN single crystal layer on a sapphire substrate by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

Detail Description Paragraph - DETX (61):

[0119] A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to  $10^{-2}$  Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to  $10^{-7}$  Torr. The sample is then heated to a temperature of 1000.degree. C. in 1 hour. The chamber is baked out to a pressure of  $10^{-6}$  Torr. Nitrogen and argon gas are then introduced into the vacuum chamber. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The plasma is ignited and set to a power of 5 kW. The system is held in this configuration for 12 hours. The plasma is then turned off and the heater is ramped to 25.degree. C. in 5 hours. During these stages, a single-crystal GaN layer is formed on the sapphire wafer as represented by, for example, layer 14 in FIG. 1 (but disregarding the illustrated buffer layer 16). The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal is

then removed from the chamber. The resulting GaN layer on the sapphire is 300 .mu.m thick and 2 inches in diameter.

Detail Description Paragraph - DETX (64):

[0121] An example of a method for manufacturing a GaN single crystal homoepitaxial layer on a GaN buffer layer on sapphire by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

Detail Description Paragraph - DETX (65):

[0122] A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to 10.sup.-2 Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to 10.sup.-7 Torr. The sample is then heated to a temperature of 1000.degree. C. in 1 hour. The chamber is baked out to a pressure of 10.sup.-6 Torr. The temperature is then reduced to 500.degree. C. in 10 minutes. Nitrogen and argon gas are then introduced into the vacuum chamber. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The plasma is turned on at 500 W for 1 minute. At this point, a GaN buffer layer is formed on the sapphire wafer as represented by, for example, intermediate layer 16 in FIG. 1. The temperature is then increased to 1000.degree. C. in 5 minutes and held for 10 minutes. The plasma is ignited again and set to a power of 5 kW. The system is held in this configuration for 12 hours. The plasma is then turned off and the heater is ramped to 25.degree. C. in 5 hours. During these stages, a single-crystal GaN layer is formed on the buffer layer as represented by, for example, layer 14 in FIG. 1. The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal is then removed from the chamber. The resulting GaN layer on the sapphire and buffer layer is 300 .mu.m thick and 2 inches in diameter.

Detail Description Paragraph - DETX (68):

[0124] Another example of a method for manufacturing a GaN single crystal layer on a sapphire substrate by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded